Extractive Distillation

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Introduction

In the first half of the twentieth century, extractive distillation (ED) became an important industrial process when World War II demanded high purity toluene for explosive production and butadiene for synthetic rubber production. Over the years, substantial developments in ED have been carried out in terms of novel solvent discovery for a particular separation, as well as the development of more sophisticated ED tower internal designs. In the petroleum and petrochemical industries, ED has been found effective in separating mixtures of aromatics/nonaromatics, diolefins/olefins, olefins/paraffins and naphthenes/paraffins.

This article will briefly review the basic concept of ED, and summarize the development of ED technologies for the applications in the following areas:

1. Aromatic purification from refining and petrochemical streams.
2. Cycloparaffin (cyclohexane or cyclopentane) recovery from naphtha or natural gas liquid.
3. Light olefins from light hydrocarbon mixtures.

The basis of ED is the increase of relative volatility between the close-boiling components caused by introducing a selective solvent, which has stronger affinity with one type of the components in the mixture. If there is a single liquid phase (no phase separation), the solvent selectivity can be measured from the experimentally observed relative volatility (α) between the key components in the presence of solvent as:

$$\alpha = (Y_1/X_1)/(Y_2/X_2)$$

where X_1 and X_2 are the mole fractions of components 1 and 2, respectively, in the liquid phase, and Y_1 and Y_2 are those in the vapour. All compositions are measured on a solvent-free basis.

In some cases, liquid-phase separation may occur in the ED tower, especially in the upper portion of the tower where less polar components are concentrated. Under this condition, the solvent phase can reject a second liquid phase, which can be defined as the raffinate liquid phase. The liquid in the solvent-rich phase is defined as the extract liquid phase. The solvent selectivity is determined by the relative volatilities of the key components in the two interrelated liquid phases and the common vapour phase, according to the following formulae:

$$\alpha_r = (\gamma_{1r} p_{1r})/(\gamma_{2r} p_{2r})$$

$$\alpha_e = (\gamma_{1e} p_{1e})/(\gamma_{2e} p_{2e})$$

where α_r and α_e are the relative volatilities of components 1 and 2, respectively, in the raffinate phase and extract phase; γ_{1r} and γ_{2r} are the activity coefficients in the raffinate phase, and γ_{1e} and γ_{2e} are the activity coefficients in the extract phase; and p_{1r}, p_{2r}, p_{1e}, and p_{2e} are the vapour pressures of the pure components (which can be estimated from an Antoine equation).

A schematic diagram of a typical ED process is presented in **Figure 1**. During a normal run, a polar, high-boiling (low volatility) solvent is introduced to near the top of the ED tower. As the nonvolatile solvent flows down the column, it preferentially associates the more polar components in the ascending vapour mixture, thus increasing the relative volatility between the polar and less polar components. The process feed stream is introduced to the middle portion of the ED tower. The more polar components are concentrated in the rich solvent, exiting the bottom of the ED tower, while the less polar components are concentrated in the overhead raffinate stream. The tower reflux stream is provided to knock down the entrained solvent from the overhead raffinate stream.

The solution, rich in polar compounds from the bottom of the ED tower, is fed to the solvent stripper, where the polar components are stripped from the solvent by heat alone or by heat and a stripping gas, such as steam. The lean solvent is then recycled to the ED tower from the bottom of the stripper.

Aromatic Purification from Refining and Petrochemical Streams

Advantages and Principle of ED Technology

Although liquid–liquid extraction (LLE) technologies have dominated the industrial processes for purifying benzene, toluene, xylene (BTX) aromatics from refining and petrochemical streams, ED technologies have gained ground quickly since the 1980s for more recent grassroots plant installations. In comparison to LLE, ED has the following advantages:

1. *Lower capital costs*. ED requires two major process units (ED tower and solvent stripper), while

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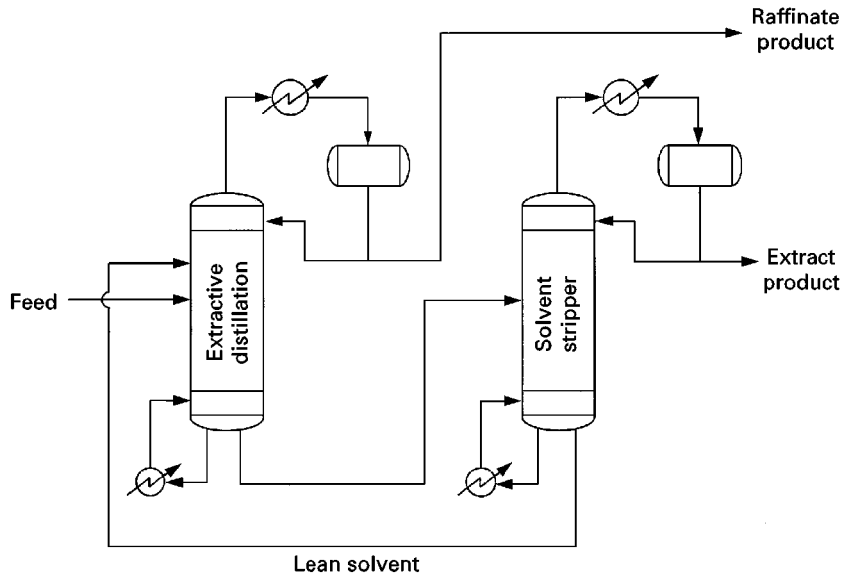

Figure 1 Configuration of an ED process.

the popular LLE, using sulfolane as the solvent, requires four major process units, including LLE tower, extractive stripper, solvent recovery column, and raffinate wash tower (see **Figure 2**).

2. *Higher operational flexibility*. LLE uses only solvent selectivity (polarity) for separation, while ED uses both solvent selectivity and boiling point for separation, so it has one extra dimension for operational flexibility.
3. *Less physical property restrictions*. Interfacial tension and density difference between the liquid phases are important concerns for LLE, but not for ED.

The principle of ED for aromatic purification was studied as early as 1944. One example was the recovery of toluene from paraffins using phenol as the selective solvent. The effect of phenol on a paraffin–toluene mixture is plotted in liquid–vapour

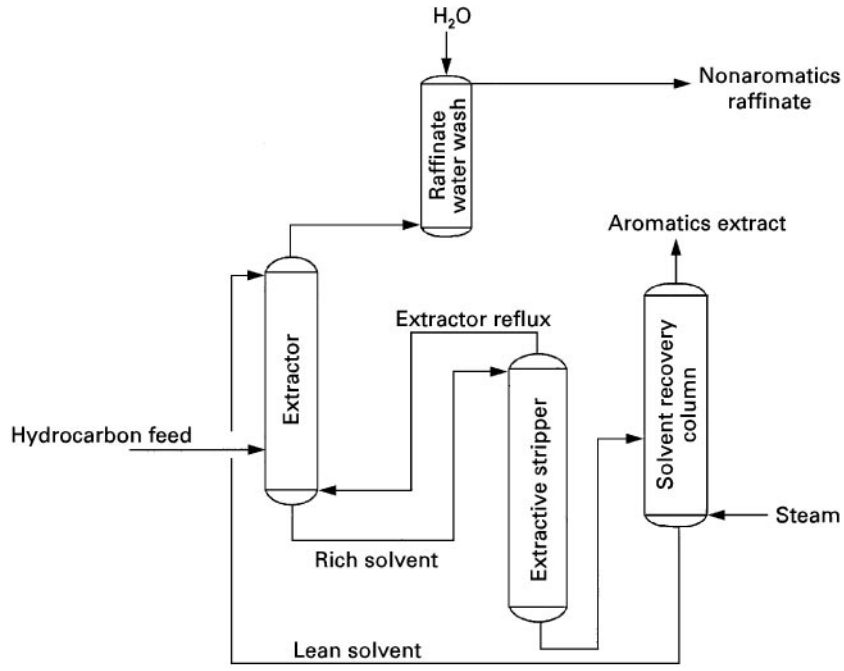

Figure 2 Configuration of liquid–liquid extraction using sulfolane for aromatic recovery.

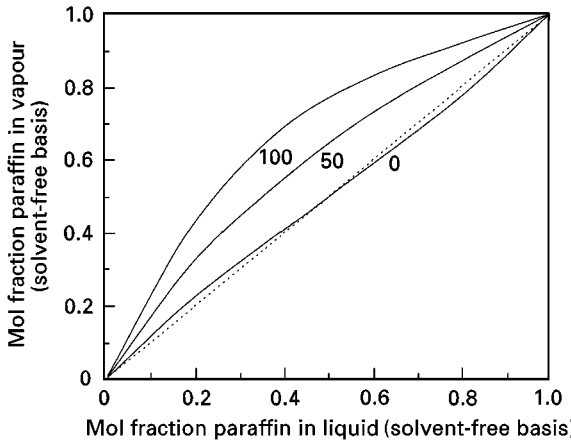

Figure 3 Effect of phenol on the vapour–liquid equilibrium of paraffin and toulene. Numbers on curves refer to mol% solvent in liquid.

diagrams as shown in **Figure 3**, in which the paraffin is considered as a hypothetical octane having the same boiling point as toluene. In the absence of phenol, there exists an azeotrope of paraffin and toluene. However, at 50 mol% phenol, the azeotrope is destroyed and the mixture is easily separated; at 100 mol% phenol, the separation between paraffin and toluene becomes very easy. **Figure 4** illustrates the effect of phenol on the change in relative volatility between paraffin and toluene. Phenol causes an increase of activity coefficient for both paraffin and toluene, but the activity coefficient of the paraffin increases to a greater extent than that of toluene. Therefore, the relative volatility of paraffin over toluene can be increased from 1.0 (no separation) to 3.7 (easy separation) at near zero hydrocarbon concentration in phenol (infinite dilution).

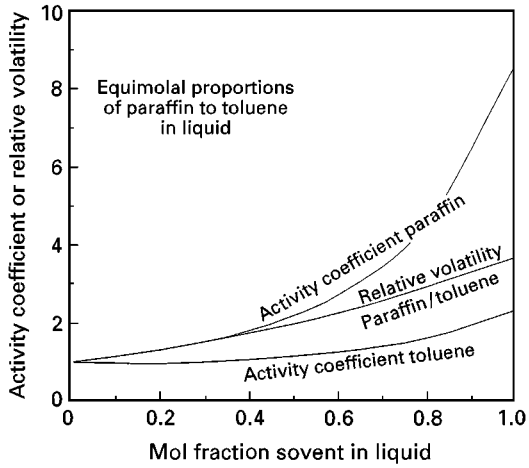

Figure 4 Effect of phenol on the activity coefficient of paraffin and toluene.

The vapour–liquid equilibria of the paraffin–toluene–phenol system were applied to test a commercial ED tower for toluene purification. As shown in **Figure 5**, the McCabe–Thiele diagram, drawn on a phenol-free basis, was used to carry out the theoretical calculations from tray to tray in the ED tower.

The calculated results were then compared with the actual results generated from a commercial ED tower with 2.1 m diameter and 65 trays. The hydrocarbon feed tray and the solvent feed tray are located at trays 19 and 39 (counted from the bottom of the tower), respectively. The tower was operated at a solvent-to-feed ratio (S/F) of 2.5, a reflux-to-overhead ratio (R/D) of 2.75, and reboiler temperature at 170°C under 1.3 atm bottom pressure. On the basis of the charge, overhead and bottoms analyses, tray-to-tray calculations were made.

Figure 6 shows the calculated concentration profiles for each component plotted against theoretical tray number. It also shows the plot of the tray analyses against actual tray number. The overall efficiencies calculated over small sections of the tower are given in **Table 1**. The average of the overall tray efficiencies throughout the tower is about 50%.

Based on the above principle, much more rigorous algorithms for tray-to-tray calculation of ED towers for multicomponent systems have been developed in

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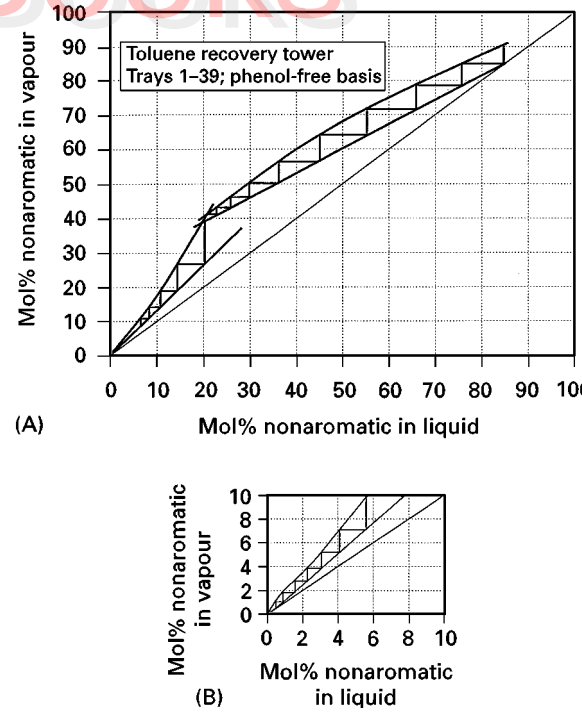

Figure 5 McCabe–Thiele diagram for paraffin and toulene separation in the presence of phenol. Part (B) is an enlargement of part of the diagram in (A).

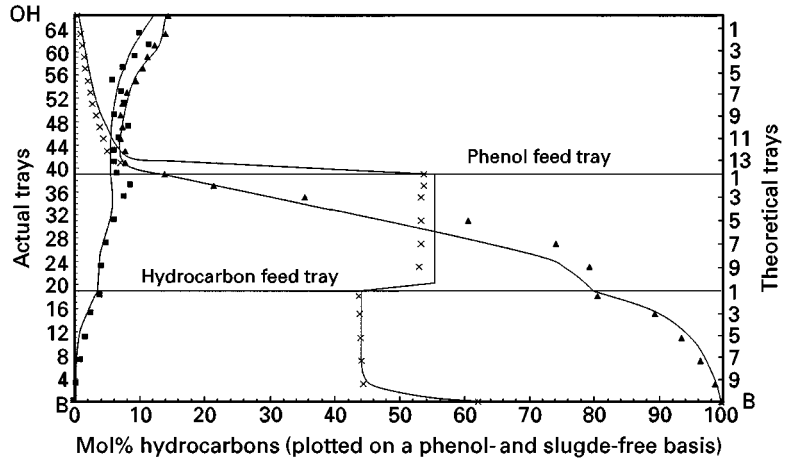

Figure 6 Calculated versus actual concentration profile of the componenets in an ED tower. Key: ■, methylcyclohexane; ▲, toluene; × phenol; ———, calculated values.

recent years, with the help of advanced vapour–liquid equilibrium theories and high-speed computers.

Handling Two Liquid Phases in ED Towers

One of the challenges of ED technology for aromatics purification is the handling of the possible formation of two liquid phases in the upper portion of the ED tower where nonaromatics are concentrated. The occurrence of a second liquid phase is due to the fact that the nonaromatics, such as paraffins, naphthenes and olefins, have significantly lower solubility in the polar solvent than aromatics.

One way to solve the problem of two liquid phases in the ED tower is to select a polar solvent that has enough solvency to dissolve both aromatics and nonaromatics in the mixture under process condition. In general, however, solvents with a high selectivity for compounds to be separated will have a reduced solvency (capacity), and vice versa. The selectivity versus solvency of the common commercial solvents for aromatic extraction is shown in **Figure 7**. Therefore, in order to eliminate two liquid phases, one may have to compromise the solvent selectivity, sometimes to a great extent.

A better way is to cope with two liquid phases in the ED tower, without sacrificing the solvent selectivity, for the following reasons:

1. Two liquid phases normally reduce the solvent selectivity in the three-phase equilibrium (vapour–liquid–liquid) condition in the ED tower. However, this can be compensated by intrinsic selectivity of a highly selective solvent. For example, the performance of sulfolane was

Table 1 Tray efficiency of ED tower for toulene purification

Section of tower trays	*Theoretical trays*	*Actual trays*	*Overall efficiency* (%)
Below phenol feed tray			
1–3	1.8	3	60.0
4–7	2.7	4	67.5
8–11	2.1	4	52.5
12–15	1.5	4	37.5
15–18	1.8	3	60.0
23–27	2.1	4	52.5
27–30	2.5	4	62.5
31–34	2.65	4	66.0
35–39	2.35	5	47.0
Above phenol feed tray			
43–65	10.8	23	47.0
49–65	8.6	17	50.7
57–65	4.5	9	50.0
61–65	2.8	5	56.0

All trays numbered from bottom of tower.

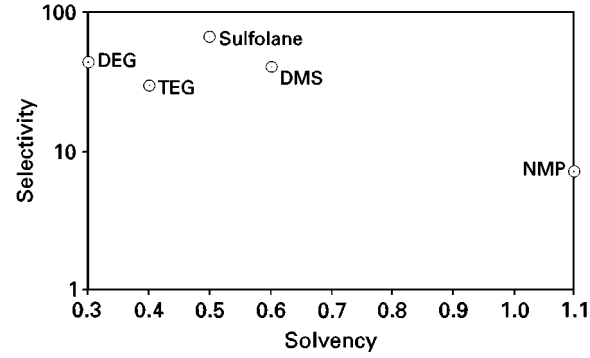

Figure 7 Selectivity versus solvency (solubility) of the common commercial solvents. DEG, diethylene glycol; TEG, triethylene glycol; DMS, dimethyl sulfoxide; NMP, *N*-methyl pyrrolidone.

compared with those of *N*-formyl morpholine (NFM) and *N*-methyl pyrrolidone (NMP). The ability of these solvents to enhance the relative volatility of *n*-heptane over benzene (an aromatic and nonaromatic separation) in a one-stage equilibrium cell was determined. **Table 2** shows that, although two liquid phases were observed using sulfolane as the solvent, sulfolane still gave a better performance than the other solvents where a single liquid phase existed in the mixture.

2. Two liquid phases have no ill effects on the efficiency of small tray or packed towers with diameter from 0.08 m to 0.46 m. However, in larger towers, the heavy liquid phase tends to accumulate on the tray if the liquid phases are not well mixed. This problem can be eliminated by tray designs promoting gas agitation, forcing the two liquid phases to behave as a homogeneous liquid. For larger packed columns, liquid–liquid redistributors are specially designed to allow separate distribution of the two liquid phases.

Computer simulations have been developed which are capable of accurately predicting the development of two liquid phases in the ED tower. In one approach, the simulation algorithm starts from linearized pressure, temperature and concentration profiles and feed conditions given by the program operator. New estimates of composition are solved, using the material balance and equilibrium relationship for each tray. Then the equilibrium constants are re-estimated and a new temperature gradient is established to calculate a tray-by-tray energy balance. Accumulated errors are calculated for the energy, material and equilibrium balances. Appropriate column operation restraints are factored in at this point. A correction factor is found for the temperature, rate profiles, and liquid composition profile by inverting the accumulated error matrix. These correction factors are used to form new iterative estimates of composition to start the process again until the correction factors are small enough to call the components converged.

Table 2 ED solvent screening for aromatics recovery

Solvent	*Relative volatility (n-heptane/benzene)*	*Number of liquid phases*
Sulfolane	3.9	2
DMSO	3.6	1
NFM	3.1	1
NMP	2.6	1

Feed: 20% *n*-heptane and 80% benzene; pressure 1 atm; DMSO, dimethyl sulfoxide; NFM, N-formyl morpholine; NMP, N-methyl pyrrolidone.

Multicomponent vapour–liquid and liquid–liquid equilibria solutions are required for the algorithm. Two activity coefficient models, NRTL (nonrandom two liquids) and UNIQUAC (universal quasichemical), are readily extendable to multicomponent systems and capable of such solutions. Experimental activity coefficients, γ, at infinite dilution are used for calculating binary parameters for the NRTL equation. These parameters are then tested using experimental liquid–liquid ternary data, experimental vapour–liquid equilibrium data, and data from pilot plant or commercial plant. The NRTL equation is used in the algorithm to calculate activity coefficients and is given in the following equations:

$$\ln \gamma_1 = x_2^2[\tau_{21}(G_{21}/(x_1 + x_2G_{21}))^2 + \tau_{12}(G_{12}/(x_2 + x_1G_{12})^2]$$

$$\ln \gamma_2 = x_1^2[\tau_{12}G_{12}/(x_2 + x_1G_{12}))^2 + \tau_{21}G_{21}/(x_1 + x_2G_{21})^2]$$

where

$$\ln G_{12} = -\beta_{12}\tau_{12}$$

$$\ln G_{21} = -\beta_{21}\tau_{21}$$

$$\tau_{12} = (\eta_{12} + S_{12}T)/RT$$

$$\tau_{21} = (\eta_{21} + S_{21}T)/RT$$

and where G_{ij}, η_{ij}, S_{ij} and β_{ij} are empirical constants, γ_i is activity coefficient, R is the gas universal constant, T is absolute temperature, and x_i is liquid phase mole fraction of component i.

The simulation uses a Newton–Raphson-based flash algorithm that checks for two liquid phases by checking Gibbs free energies for components the program operator lists as possible second liquid phase formers. If two liquid phases are indeed present, regular solution theory provides a method of combining the liquid-phase activity coefficients.

State-of-the-art ED Technologies

The modern state-of-the-art ED technologies for BTX aromatic purification are based on several solvent systems: sulfolane, NFM and NMP. Proprietary cosolvents may be blended into the base solvent to enhance the performance in specific applications.

Table 3 summarizes the key performance parameters of LLE and ED for aromatics recovery. ED process can provide up to 25% savings in capital investment as compared with the commercially available LLE processes. This saving is attributable to the

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Table 3 Comparison of aromatic recovery technologies

System	*UDEX™*	*Arosolvan™*	*Sulfolane™*	*Morphylane®*	*GT-Aromex™*
Solvent	Tetra-EG	NMP	Sulfolane	N-formyl morpholine	Proprietary
ISBL capital cost (million US$)	9.5	11.0	10.7	11.0	8.1
Utilities					
Power (kWh per t of feed)	—	6.6	2.4	4.6	4.8
Steam (kcal per kg of feed)	211	225	177	250	194
Cooling H_2O (gal per lb of feed)	19	—	—	16	21
Aromatics recovery					
Benzene	99.9%	99.9%	99.9%	99.9%	95.0%
Toluene	99.5%	99.5%	99.0%	99.5%	99.5%
Xylene	95%	95%	95%	97%	100%
Solvent-to-feed ratio (v/v)	4 : 1	0.4 : 1	2 : 1	3 : 1	3 : 1

Data are for 1994 construction, extraction section only; all processes are pro rata for 1600 metric tons day^{-1} reformate feed; sources include SRI International, Handbook of Solvent Extraction, Petroleum Refining Technologies & Economics, and licensor literature.

smaller number of operating units, as mentioned above. The ED process recovers more xylenes but less benzene than LLE processes.

The Morphylane® process offered by Krupp Koppers uses NFM as the selective solvent. A schematic diagram of the Morphylane® process is given in **Figure 8**. The diagram is very similar to the general ED process scheme as shown in Figure 1, except the nonaromatic vapour exiting the top of the ED tower contains a small amount of NFM solvent (0.9 wt%), which must be recovered. Two methods are used for this solvent recovery, both of which require additional equipment and expense: (1) a separate solvent recovery column; and (2) additional trays or packings fitted to the top of the ED tower (above the solvent tray), using nonaromatics as the reflux to flush NFM back into the ED tower. To use the second method, the feedstocks to the ED tower must contain only very small amounts of critical components, such as methylcyclohexane and dimethylcyclopentane in pyrolysis gasoline feedstock, or C_7 olefins in reformate feedstock.

The Morphylane® process is available in commercial applications for recovering high purity benzene from C_6 fraction, or pure benzene and toluene from the C_6–C_7 fraction of reformate or pyrolysis gasoline. For example, the process has been commercially tested with a feedstock from a mixture of C_6 reformate fraction and a C_6 fraction of a pyrolysis gasoline. The plant had a top-fitted solvent recovery system. The results are summarized in **Table 4**. Approximately 98% benzene recovery with 99.9% benzene purity was achieved with this process. This process, however, has not been applied to the recovery of higher

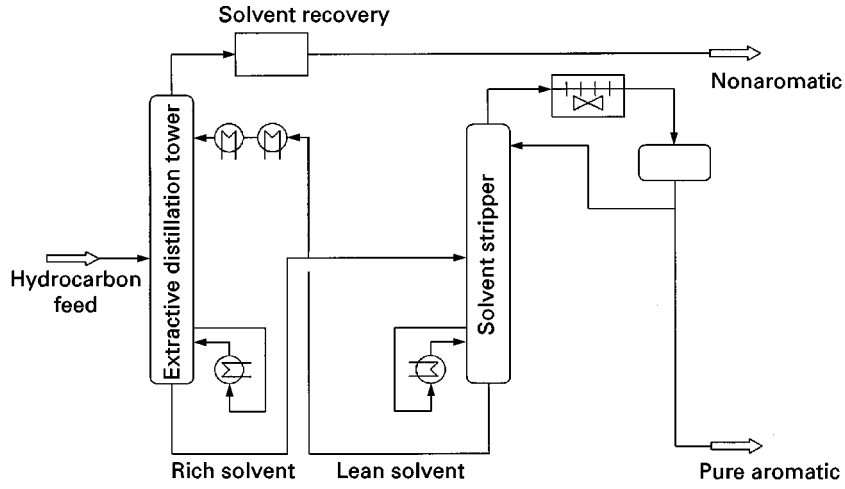

Figure 8 Schematic diagram of the Morphylane® process for aromatic purification.

Table 4 ED performance for benzene recovery from the C_6 fraction

Parameter	*Units*	*Value*
Throughput	$t\,h^{-1}$	23.0 (approx. 116%)
Benzene production	$t\,h^{-1}$	12.89
Benzene purity	wt %	99.98
Benzene yield	wt %	98.11
Solvent consumption	$g\,t^{-1}$ aromatics	6.0
Solvent in benzene product	ppm	Not ascertainable
Steam consumption (16×10^5 Pa) (including benzene column)	$kg\,t^{-1}$ feed	564
Energy consumption for extractive distillation only 16×10^5 Pa steam	$kg\,t^{-1}$ feed $Gcal\,t^{-1}$ feed	349 0.161

boiling aromatics, such as mixed xylenes or C_9^+ and higher aromatics, probably because of the relatively low boiling point of NFM.

The GT-BTX^{SM} process offered by GTC Technology Corporation is available for recovering not only benzene and benzene/toluene, but also a full range of aromatics (benzene, toluene and xylenes) with high purity and recovery. The process uses a proprietary sulfolane-based solvent blend. Due to the high boiling point of the solvent, the process is very effective in recovering higher boiling aromatics, such as xylenes and C_9^+ and higher aromatics. Unlike the Morphylane® process, the overhead nonaromatics stream from the ED tower in the GT-BTX^{SM} process contains essentially no solvent, and does not require a separate solvent recovery tower.

A hybrid concept of the GT-BTX^{SM} process can be used to increase substantially the capacity of the liquid–liquid extraction unit and improve the quality of the benzene product, through retrofitting of the existing unit. The retrofitting can be carried out using this hybrid concept without requiring extensive modifications, investment or lengthly shutdown time. **Figure 9** shows a new process using a hybrid of the sulfolane liquid–liquid extraction process with the GT-BTX^{SM} process that bypasses part of the feed around the original extraction section. In the hybrid scheme, the ED tower is better suited to purifying the benzene-rich feed than the liquid–liquid extraction unit, and it is not subject to the maximum aromatics limit in the hydrocarbon charge. The ED tower nonaromatic stream (rich in cyclohexane) may be recycled to the reformer unit for producing more benzene, while the raffinate stream from the liquid–liquid extractor (rich in paraffins) could be routed to gasoline blending or used as a feedstock for naphtha cracking to produce ethylene and pyrolysis gasoline. The major changes are modifications of the solvent system to be compatible with both extraction operations and to make the appropriate tie-ins to the ED tower.

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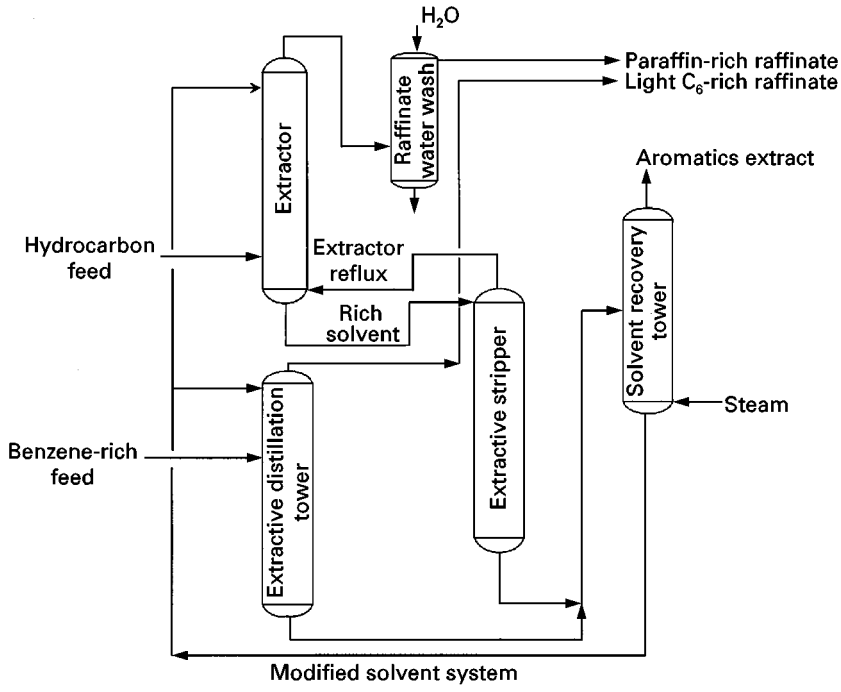

Figure 9 Hybrid scheme for aromatic recovery process expansion.

Cyclohexane Recovery from Naphtha or Natural Gas Liquid

In recent years, ED technology has also been applied to the separation of paraffins and cycloparaffins, a much more difficult separation than aromatics and nonaromatics. One of the major developments was cyclohexane recovery from naphtha or natural gas liquid (NGL) streams. Cyclohexane, an important raw material for the nylon industry, exists naturally in naphtha and NGL streams. However, recovery of high purity cyclohexane from naphtha or NGL through conventional distillation is virtually impossible, owing to the close-boiling C_7 isomers in the streams. Since the polarity difference between cyclohexane and C_7 isomers is substantially smaller than that for aromatic and nonaromatic compounds, no extractive solvent has been found that can effect the separation. However, through the use of a cosolvent (to enhance the solvency of the mixed solvent), an ED process has been commercialized to recover high purity cyclohexane directly from an NGL fraction containing 85% cyclohexane.

Many solvent blends show synergistic improvement over what would be expected by pure component mixing. To test the concept, experiments were conducted in a one-stage vapour–liquid equilibrium (VLE) cell to compare the selectivity of five solvents. To a hydrocarbon mixture of 85 wt% cyclohexane (C_yC_6) and 15 wt% 2,3 dimethylpentane (2,3-DMP), a selective solvent or a mixed solvent was added, at a solvent-to-feed ratio (S/F) of 7.0. The relative volatility of 2,3-DMP over C_yC_6 was measured in the equilibrium cell with various solvents. **Table 5** presents a comparison of relative volatilities obtained for five solvents tested, including a proprietary mixed solvent (MIST) from Phillips Petroleum Company. MIST solvent, discovered by investigating the combinations of many other solvents, has a significantly higher relative volatility than the other single solvents.

Computer simulations were carried out to confirm the results on solvent screening from the one-stage VLE cell for the mixed and single solvents shown in Table 5. These simulations were based on experimental physical property data, such as the infinite dilution activity coefficients of binary solvent–hydrocarbon mixtures. Again, NRTL thermodynamic correlations were used to predict the occurrence of two liquid phases and a Newton–Raphson convergence method was used to carry out the simulations.

Table 5 Equilibrium cell study for C_yC_6 and 2,3-DMP separation

Solvent	*No. of liquid phases*	*Relative volatility (2,3-DMP/C_yC_6)*
(No solvent)	1	0.84
EG	2	1.02
TEG	2	1.06
Sulfolane	2	1.07
NMP	1	1.07
MIST	1	1.22

Table 6 Computer simulation for solvent comparison

Solvent	*2,4-DMP recovery (%)*	*C_yC_6 purity (wt%)*	*Separation factor*[a]
MIST	85.5	97.5	586
TEG	53.7	92.4	115
Sulfolane	51.7	92.1	106
NMP	45.9	91.2	84
EG[b]	0.0	85.0	0

[a]Separation factor $= \dfrac{\text{mole fraction 2,4-DMP raffinate/mole fraction } C_yC_6 \text{ raffinate}}{\text{mole fraction 2,4-DMP extract/mole fraction } C_yC_6 \text{ extract}}$.

[b]Simulation failed to converge.

Premises: 99% C_yC_6 recovery, overhead product allowed to vary; S/F weight ratio = 16; 25 equilibrium stages (solvent fed on stage 24, hydrocarbon fed on stage 12); reflux fixed at 0.48 (hydrocarbon feed).

Simulations of a ED process separating an 85/15 wt% C_yC_6/2,4-DMP mixture were made to compare the MIST solvent with four common extraction solvents, ethylene (EG), triethylene glycol (TEG), sulfolane and *N*-methyl pyrrolidone (NMP). The simulations were for a 25 theoretical stage ED tower at a S/F ratio of 16. The C_yC_6 recovery in the extract stream was specified at 99.0% and the overhead raffinate product was allowed to vary. **Table 6** shows that the MIST solvent has a separation factor 5 times greater than TEG, which has the highest separation factor of the single solvents.

The MIST solvent was first tested in a 150 mm diameter ED pilot plant using as the feedstock a refinery stream that had an average composition as shown in **Table 7**. Based on the successful pilot plant study, a commercial plant purifying 100 metric tonnes per day cyclohexane was designed, constructed and commissioned in 1991.

Light Olefin and Paraffin Separations

The synthetic rubber process, brought to a successful culmination during World War II, required large quantities of butadiene; consequently normal

Table 7 Average ED pilot plant feedstock

Components	*wt%*
Cyclohexane	89.1
2,2-Dimethylpentane	1.3
2,4-Dimethylpentane	4.0
3,3-Dimethylpentane	0.1
2,3-Dimethylpentane	0.9
2-Methylhexane	1.6
3-Methylhexane	1.1
2,2,3-Trimethylbutane	0.8
Dimethylcyclopentanes	1.0
n-Heptane	0.1

butenes, the feedstock to butadiene units, were also in great demand. ED process technology was developed to recover high purity *n*-butenes suitable for producing butadiene to feed the synthetic rubber process. In this case, the selective solvent, developed by Shell Development Company in Houston, Texas, USA, was a mixture of 85% acetone and 15% water.

Later, furfural was used as an ED solvent for separating isobutane from butene-1, *n*-butane from butene-2, and butene-1 from butadiene. As shown in **Figure 10**, furfural was tested in an ED tower consisting of two 50-tray sections in series for separating butene-2 from *n*-butane. Solvent was charged to a tray, which was several trays from the top of the first section (A), and flowed to the bottom of this section. It was pumped together with dissolved hydrocarbons to the top of the second section (B), and withdrawn from the bottom of this section together with hydrocarbon bottoms. The solvent and bottoms are separated in a smaller 20-tray stripper tower, the solvent-free bottoms being removed as overhead and stripped solvent circulated back to the ED tower. Hydrocarbon feed is charged at some point below the solvent feed, near the bottom of the first section or top of the second section of the ED tower.

For *n*-butane and 2-butene separation, the purity of 2-butene was 94.6 vol% with only 39.4 vol% recovery. For mixed butanes and mixed butenes separation, the purity of mixed butenes was 88.7 vol% with 96.7 vol% recovery, and for butadiene and butenes separation, the purity of butadiene was 96.9 vol% with 89.7 vol% recovery. Obviously, these results did not meet the industrial requirements for producing high purity product with high recovery.

Further studies were carried out to screen solvents for olefin and paraffin separations. For example, a comprehensive solvent screening study was conducted for *n*-butane and butene-2 separations. Eighty solvents were evaluated, including ester-type solvents containing hydroxyl groups, aldehyde groups, amine groups, nitrile groups, nitro groups, ketone groups, nitrogen; ether-type solvents; and miscellaneous solvents. It was found that aniline and furfural were the most selective solvents. The VLE data for *n*-butane and 2-butenes in furfural and aniline solvents are given in **Figures 11** and **12**. Although *N*-formyl morpholine was also tested among the nitrogen-containing solvents for *n*-butane and 2-butenes separation,

DropBooks

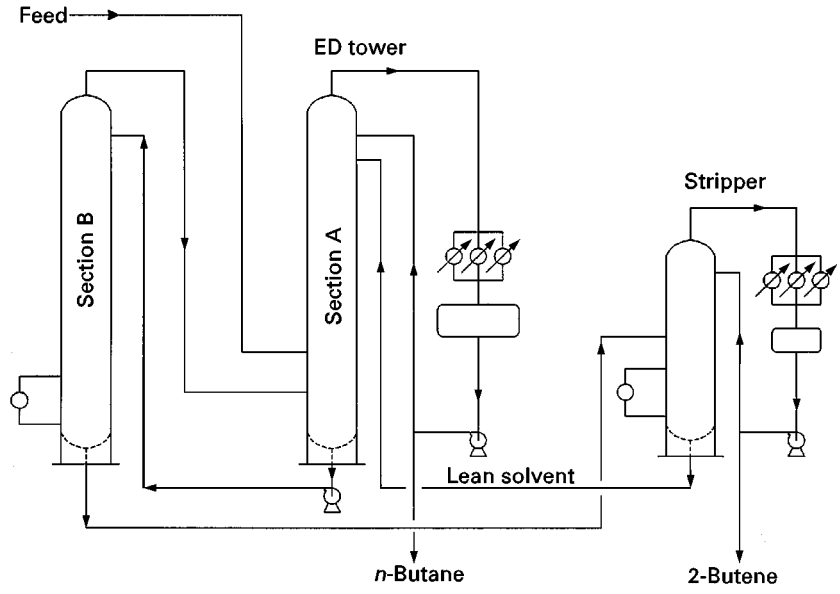

Figure 10 Schematic ED process diagram for separating 2-butene and *n*-butane.

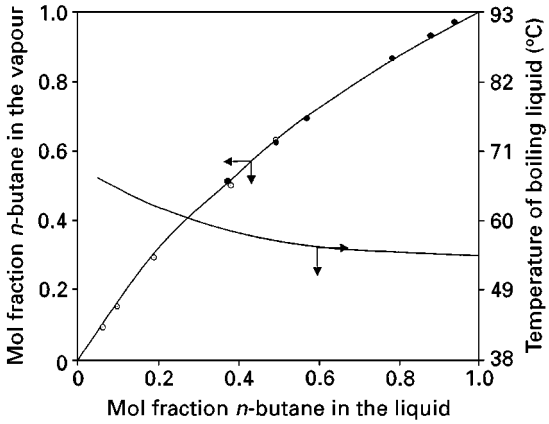

Figure 11 Vapour–liquid equilibrium of *n*-butane and 2-butene in Furfural. Solvent dosage: ●, 3.7; ⊙, 4.5. Pressure, 3862 mmHg.

for unknown reasons the solvent was not considered for commercialization until recently.

Krupp Koppers has offered the BUTUNEX process, an ED process using *N*-formyl morpholine as the selective solvent, for recovering 1-butene and 2-butene from C_4 hydrocarbon streams. On the basis of such a feedstock with the composition of 25.6% isobutane, 32.7% *n*-butane, 26.6% 1-butene and 15.1% 2-butene, the following yields can be achieved:

1-Butene	95.6%
2-Butene	99.1%
Butanes	98.9%

The purity of 1-butene and 2-butene products can be 99.6% and 95.9%, respectively.

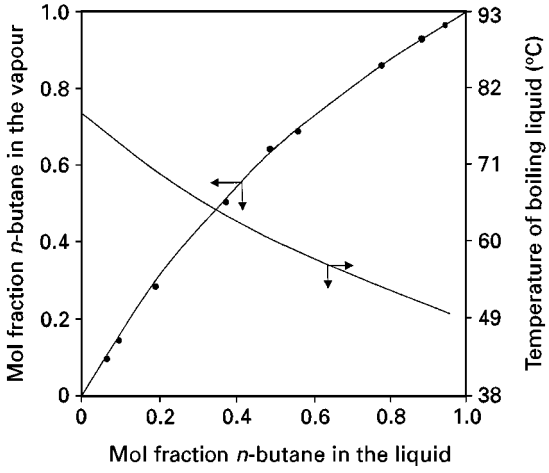

Figure 12 Vapour–liquid equilibrium of *n*-butane and 2-butene in aniline. Solvent dosage, 5.0; pressure, 3862 mmHg.

Conclusions

Since the 1940s, ED technology has gone through extensive development for solving many difficult separation problems in the petroleum and petrochemical industries. The development in cosolvent selection tailored for a specific separation and the advancement in tower internal design have made ED a competitive process. In many cases, ED processes can be more efficient and economical than conventional LLE in terms of capital investment, energy consumption and ease of operation. It is anticipated that the ED technology will be selected more frequently in the future for the petroleum and petrochemical industries.

See also: **II/Distillation:** Theory of Distillation. **III/Reactive Distillation.**

Further Reading

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